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CAPACITOR POWDER

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## Abstract

The invention relates to capacitors, which contain vanadium, are based on niobium, and which comprise a BIAS-independent capacitance.

This invention concerns a powder for the production of electrolytic capacitors, in particular a powder for production of anodes for electrolytic capacitors.

The "earth acid" metals niobium and tantalum in particular are described in the literature as starting materials for the production of such capacitors. The capacitors are produced by sintering the finely divided powders to form pellets, producing a structure with high surface area, followed by anodic oxidation of the surface of these sintered elements to produce a

nonconductive insulating layer (dielectric) and application of the counterelectrode in the form of a layer of manganese dioxide or a conductive polymer. The particular suitability of the "earth acid" metal powders derives from the high relative dielectric constants of the pentoxides.

Only tantalum powder is currently of industrial importance for capacitor production. This is due on the one hand to the ability to manufacture finely divided tantalum powder with a batch-to-batch reproducibility manner and on the other hand to the fact that the insulating oxide layer of tantalum pentoxide has especially pronounced stability. This is possibly due to the fact that, in contrast to niobium, tantalum does not form a stable suboxide.

To be sure, the disadvantages of tantalum are becoming increasingly important in the course of the rapid development of microelectronics. Tantalum is among the rare metals (54th in natural frequency of elements in the earth's crust, at 2.1 g/t) with few workable deposits (only hard rock mining) and, moreover, tantalum ores contain only very low concentrations of tantalum. For example, the typical tantalum ores being mined today (for example, in Australia) frequently contain less than 0.1%  $\text{Ta}_2\text{O}_5$  (about 300 ppm Ta).

On the other hand, niobium, which is situated above tantalum in the same group of the periodic system and is very similar in behavior to tantalum, is 10-12 times more common (33rd in natural frequency of elements in the earth's crust, at 24 g/t) and occurs in more readily workable deposits. Commercially the most important deposits are in Brazil (78% of world reserves), where ore containing over 3%  $\text{Nb}_2\text{O}_5$  is strip mined. Other deposits are found in Canada, Nigeria and Zaire. Finally, the price of raw materials for niobium ore concentrates is distinctly lower than for tantalum ore concentrates and, moreover, is not subject to such severe fluctuations.

In addition, there is a natural limit of growth for the specific capacitances of tantalum powder that can be reached. To achieve higher capacitances  $C$  in the case of Ta powder, the specific surface has to become greater ( $C = \epsilon_0 \epsilon_r \cdot A/d$ ), which for a given powder particle geometry involves size reduction of the particles. If the average particle size for an anodically generated dielectric layer in the nanometer range likewise lies in the nanometer range, regions of the metallic sintered element become "anodized through," i.e., in particular in thin regions such as sinter necks between two particles there is no longer any metallic conductivity present. In this way partial regions of the anode become inactive.

Moreover, the sensitivity of tantalum powders to oxidation increases sharply with increasing powder particle size and accordingly with an increase of the specific surface.

For these reasons and because of the clearly higher dielectric constant of niobium ( $\epsilon_r \sim 42$ ) compared to tantalum ( $\epsilon_r \sim 27$ ), it has been the goal of many researchers to develop niobium

capacitors. However, the use of niobium capacitors up to now has remained restricted to the range of low specific capacitances with low specific surfaces and lower quality.

One reason for this is that pure niobium has two disadvantages over tantalum with regard to capacitor applications. For one thing the tendency of the anodically produced oxide film to field crystallization is more highly pronounced than with tantalum. The radial growth rate of crystalline areas is specifically 1000 times greater than for tantalum under the same anodization conditions (N. F. Jackson, J. C. Hendy, *Electrocomponent Science & Techn.* 1974, 1, 27-37), which can, however, for the most part be suppressed by conducting anodization at lower temperatures (Y. Pozdeev: "Comparison of tantalum and niobium solid electrolytic capacitors" TIC 1997; films must be amorphous; crystalline regions in the film have elevated conductivity). The other disadvantage concerns the greater sensitivity of anodically produced  $\text{Nb}_2\text{O}_5$  films to heat treatment.

One step in the production of solid electrolytic capacitors is the application of the semiconductive cathode material  $\text{MnO}_2$ . This takes place by immersing the anode bodies in manganese nitrate solutions to produce a thin  $\text{MnNO}_3$  layer, which is then thermally decomposed to  $\text{MnO}_2$ . Here the Ta- $\text{Ta}_2\text{O}_5$  system is subjected to temperatures between 250 and 450°C for 10-30 min. This heat treatment can, however, lead to an increase of the dependency of the capacitance on frequency, temperature and bias. The fact that at temperatures over 300°C the tantalum substrate can withdraw oxygen atoms from the anodically produced tantalum oxide layer, which leads to an exponential gradient of oxygen holes in the oxide film, is seen as a cause of this. These holes cause a shift in the conductive behavior of the oxide film from a dielectric to an n-semiconductor or, if the holes are present in a sufficiently high concentration, to a conductor. This is shown schematically in Figure 1. The critical conductivity  $\sigma_0$  separates the insulating from the conducting part of the oxide film. If the temperature is elevated, the semiconducting layer in the oxide film spreads and the effective insulating layer becomes thinner. Independent of the temperature dependency of the dielectric constant, this gives rise to an increase of the capacitance. In such a case the application of an anodic bias voltage causes electrons to flow from the holes into the tantalum metal. This results in the formation of an electric double layer, which is defined on the metal side by electrons at the interface and on the semiconductor side by the positive space charge in a boundary layer that is depleted of charge carriers (Schottky-Mott barrier). This causes the increase of the conductivity gradient to be even greater and results in an increase of the effective thickness of the dielectric, but which, in accordance with  $C = \epsilon_0 \epsilon_r \cdot A/d$ , is accompanied by a decrease of the capacitance.

While anodically produced oxide films on tantalum are dielectric and do not exhibit semiconducting regions until higher temperatures are reached, anodically produced oxide films

on niobium already behave like n-type semiconductors at room temperature (A. D. Modestov, A. D. Dadydov, *J. Electroanalytical Chem.* 1999, 460, pp. 214-225) and exhibit a Schottky barrier at the  $\text{Nb}_2\text{O}_5$ /electrolyte interface (K. E. Heusler, M. Schulze, *Electrochim. Acta* 1975, 20, p. 237; F. Di Quarto, S. Piazza, C. Sunseri, *J. Electroanalytical Chem.* 1990, 35, p. 99). The reason for this could be that niobium, in contrast to tantalum, forms various stable suboxides. For example, it is known from the literature that with oxide films on niobium only the outer layer consists of  $\text{Nb}_2\text{O}_{5-x}$  (M. Grundner, J. Halbritter, *J. Appl. Phys.* 1980, 51(1), pp. 397-405), which moreover is not really stoichiometrically composed and has an excess of oxygen  $x$ . Between the  $\text{Nb}_2\text{O}_{5-x}$  layer and the niobium metal substrate there is a layer of NbO, since this is the thermodynamically stable phase in contact with the oxygen-saturated niobium metal, and not the pentoxide as in the case of tantalum (K. E. Heusler, P. Schlüter, *Werkstoffe & Korrosion* 1969, 20(3), pp. 195-199).

The oxygen content of the surface passive layer in the case of niobium is about 3500 to 4500 ppm per  $\text{m}^2$  specific surface. When Nb anodes are sintered, the oxygen of the surface passive layer diffuses into the metal and becomes uniformly distributed there. In this case the thickness of the NbO layer also increases in proportion to the surface of the powder that is used, which can be followed very easily by X-ray diffraction on sintered niobium anodes. In an extreme case, when there is a very high specific surface and thus very high oxygen content in the powder, this results in the anode body chiefly consisting of NbO and no longer of niobium metal after sintering. However, in contrast to tantalum, this increase of oxygen does not become felt in a significant increase of the leakage current of anodes of such powders.

Another point is that the  $\text{MnO}_2$  cathode operating as solid electrolyte acts as an oxygen donor and can compensate the oxygen deficiency in the  $\text{Nb}_2\text{O}_{5-x}$  layer. However, this is not a steady process, since as this happens lower, nonconductive manganese oxide phases ( $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$ ,  $\text{MnO}$ ) arise in the vicinity of the  $\text{MnO}_2/\text{Nb}_2\text{O}_5$  interface and these suppress further oxygen diffusion from the  $\text{MnO}_2$  cathode to the semiconducting  $\text{Nb}_2\text{O}_{5-x}$  layer. This leads to an increase of the number of holes  $x$ , to accelerated increase of leakage current and finally to failure of the capacitor (Y. Pozdeev in *Carts-Europe '97: 11th European Passive Components Symposium*). For this reason niobium capacitors should have a clearly lower lifetime than tantalum capacitors.

This semiconducting behavior of the anodically produced barrier layer on niobium has the consequence that to measure the correct capacitance values of niobium anodes that will be achieved subsequently in the finished capacitor it is necessary to apply a positive bias to them, since otherwise it will not be possible to obtain a sound measurement and values that are much too high will be mistakenly obtained.

By comparison measurements of the capacitance of anodes of niobium metal, niobium(II) oxide and also niobium/tantalum alloys (90:10, 80:20, 70:30) and those of capacitors made from these materials, it was established that an anodically applied bias voltage of  $\geq 1.5$  V is necessary in order to measure correct capacitance values for the anodes that are correct and will also be repeated subsequently in the finished capacitor and that capacitances of such anodes measured without the applied bias voltage will be 3-4 times higher than ones measured with a bias voltage of at least 1.5 V, thus false values will be mistakenly obtained. Accordingly, for the specific leakage current with reference to capacitances measured without bias values result that are 3-4 times lower than the actual specific leakage current.

A very important characteristic for the suitability of a powder as capacitor material is its chemical purity, since both metallic as well as nonmetallic contaminants can lead to defects in the dielectric layer or to lower stability of it. In particular, the elements Na, K, Fe, Cr, Ni and C should be viewed as critical for the leakage current of tantalum anodes. Through the continuous improvement of Ta powders these contaminants today are at the vicinity of the detection limits with the powders produced by sodium reduction of  $K_2TaF_7$ .

The corresponding process via  $K_2NbF_7$  in contrast is not available for the production of highly pure niobium powders, since the retort material becomes partially dissolved because of the high corrosivity of the corresponding heptafluoronioate salts and the resulting niobium powders are highly contaminated with Fe, Cr, Ni, etc. Furthermore, the so-called EB powders, which are produced by embrittlement of an electron beam melted niobium ingot with hydrogen, grinding, and subsequent dehydration are also unsuitable for the production of high capacitance in the capacitors. If the grinding just described is carried out in an attrition mill under alcohols, for example, one obtains niobium flakes, which, however, mostly have a very high degree of metallic contaminants like Fe, Cr, Ni and C that become incorporated into the niobium powder in the grinding process through mechanical alloying and subsequently can no longer be washed out with mineral acids.

However, the niobium powders obtained by two-stage reduction of niobium pentoxide with hydrogen or gaseous magnesium in accordance with the published proposals of the applicants as in DE 19831280 A1 or WO 00/67936, are very pure. These powders contain metallic contaminants such as Fe, Cr, Ni, Al, Na, K, in amounts of  $<25$  ppm.

Besides chemical purity, which is crucial for electrical properties, a capacitor powder also has to satisfy certain requirements on physical properties. For example, it must have a certain flowability, so that it can be processed using the completely automatic anode presses of the capacitor manufacturer. In addition, the pressed anode bodies must have a certain green strength,

so that they do not immediately fall apart again, and sufficiently high pore distribution in order to ensure complete impregnation with manganese nitrate.

The task of this invention is to overcome the disadvantages of the known niobium-based capacitors that were described above. In particular, it is a task of this invention to improve the insulating behavior and thermal stability of the niobium pentoxide barrier layer of niobium-based capacitors so that higher lifetimes combined with higher capacitances and lower leakage currents can be achieved with such capacitors.

It was now found that such niobium-based capacitors exhibit clearly improved properties of the anodically produced oxide film by alloying/doping at least the barrier layer with vanadium. It was found in particular with the help of impedance spectroscopic measurements and evaluation of Schottky-Mott diagrams that the whole concentration is clearly reduced in the anodically produced oxide layers of such capacitor anodes and is similarly low to that in the corresponding  $\text{Ta}_2\text{O}_5$  layers. Furthermore, there are initial indications of long-term stability compatible with that of tantalum anodes, which cannot be achieved with traditional niobium-based capacitors.

An object of the invention is accordingly capacitors with an anode based on niobium and a barrier layer based on niobium pentoxide, where at least the barrier layer contains vanadium.

Niobium-based capacitors in the sense of this invention are capacitors that have an anode of sintered finely divided niobium-based powders, where "niobium-based" includes electrically conductive compounds and alloys whose primary component is niobium, as well as niobium metal. Suitable compounds are, for example, niobium oxides  $\text{NbO}_x$ , with  $x = 0-2$ , niobium nitride, or niobium oxynitride. Suitable niobium alloys are in particular Nb/Ta alloys with a niobium content of at least 50 wt%.

In accordance with the invention niobium metal (with an oxygen content, governed by manufacture, of 3000-4500 ppm per  $\text{m}^2$  specific surface) and  $\text{NbO}_x$  with  $x = 0.8-1.2$  are preferred.

Other preferred niobium-based capacitors have a niobium core, a niobium suboxide intermediate layer and a niobium pentoxide dielectric.

Preferably, the vanadium content of such niobium-based capacitors is 10-100,000 ppm (weight) with respect to niobium and optionally tantalum. In particular, the vanadium content is preferably 200-20,000 ppm.

The capacitor anodes based on vanadium-containing niobium in accordance with the invention are characterized by capacitance that is essentially independent of bias, i.e., an anodically connected d.c. voltage that is superimposed on the a.c. voltage for measurement of the capacitance. An object of the invention are also niobium-based capacitor anodes that contain



vanadium. Preferably, the anodes contain 10-100,000 ppm vanadium with respect to niobium and optionally tantalum. Especially preferably the vanadium content is between 200 and 20,000 ppm.

Another object of the invention consists of powders based on niobium that contain 10-100,000 ppm, preferably more than 200 ppm, especially preferably 500-20,000 ppm vanadium, with respect to niobium and optionally tantalum.

Additionally preferably, the niobium-based powders have Fe, Cr, Ni, Al, Na and K contents of less than 25 ppm each, especially preferably less than 100 ppm altogether.

An object of the invention is also a preferred method for producing the vanadium-doped/alloyed niobium-based powders in accordance with the invention. This method consists of mixing vanadium, a vanadium oxide or a vanadium compound that can be hydrolyzed or thermally decomposed to vanadium oxides in solid or dissolved form in the appropriate ratio with Nb, Nb<sub>2</sub>O<sub>5</sub>, NbO<sub>2</sub> or niobium oxide hydrate Nb<sub>2</sub>O<sub>5</sub>·xH<sub>2</sub>O powders, calcining the mixture, optionally after drying, and then reducing the mixed oxide to suboxide or metal and optionally nitriding it.

All vanadium oxides like V<sub>2</sub>O<sub>5</sub>, VO<sub>2</sub>, V<sub>2</sub>O<sub>3</sub> and VO are suitable as vanadium compounds, with V<sub>2</sub>O<sub>5</sub> being especially preferred. In addition, all vanadium compounds that can be hydrolyzed or thermally decomposed to oxides, such as ammonium metavanadate, vanadium(IV) oxide acetylacetonate, vanadium(IV) oxide sulfate pentahydrate, vanadium halides, etc., are also suitable. Ammonium metavanadate is especially preferred.

Preferably, finely divided powders of Nb<sub>2</sub>O<sub>5</sub>, especially preferably niobium oxide hydrate Nb<sub>2</sub>O<sub>5</sub>·xH<sub>2</sub>O, are used as niobium component.

Highly porous powders that were obtained by the published proposals of the applicant in accordance with US 6,171,363 B1, DE 19831280 A1, DE 19847012 A1 and WO 00/67936 by reduction of niobium pentoxide in liquid or gaseous magnesium, optionally after prior reduction to suboxide by means of hydrogen, are especially suitable as niobium powders.

If the calcination with vanadium oxides takes place by using Nb<sub>2</sub>O<sub>5</sub> or Nb<sub>2</sub>O<sub>5</sub>·xH<sub>2</sub>O, the reduction for preparation of vanadium-containing Nb<sub>2</sub>O can take place by heating to 950-1500°C in a hydrogen atmosphere.

The reduction of vanadium-containing NbO<sub>2</sub> or Nb<sub>2</sub>O<sub>5</sub> to a vanadium-containing Nb metal powder preferably takes place in accordance with DE 19 831 280 A1, DE 19 847 012 A1 or PCT/US 99/09 772. Reduction by means of magnesium vapor under a protective gas atmosphere in a solid bed is preferred. The reduction especially preferably takes place in a fluidized bed with argon as carrier gas, where the carrier gas before being introduced into the

fluidized bed reactor is passed through a magnesium melt at a temperature close to the boiling point of the magnesium.

The reduction of the calcination product of  $\text{Nb}_2\text{O}_5$  or  $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  and vanadium oxide or V-containing  $\text{NbO}_2$  to vanadium-containing  $\text{NbO}$  can also advantageously take place by mixing the vanadium-containing  $\text{NbO}_2$  or  $\text{Nb}_2\text{O}_5$  powder with (preferably likewise vanadium-containing) Nb metal powder and then heating it to temperatures between 950 and 1600°C in a stream of hydrogen or in a vacuum.

To produce nitrided or oxynitrided vanadium-containing niobium-based powders the vanadium-containing niobium metal powder or  $\text{NbO}_x$  powder, preferably with  $x = 0.1-0.5$ , is heated up to 1000°C in a nitrogen-containing atmosphere.

The niobium-based capacitor powders in accordance with the invention preferably have primary particle sizes from 300 to 1500 nm, especially preferably 400-600 nm. The powders are preferably used in the form of agglomerates with particle sizes from 40 to 400  $\mu\text{m}$ . To establish the agglomerate size, it is possible to carry out a deoxidizing agglomeration by heating to 800-1000°C in the presence of a small amount of magnesium followed by grinding through a screen with mesh of 250-400  $\mu\text{m}$  in a substantially known way.

The further processing to capacitor anodes takes place by compression molding and sintering at 1050-1350°C up to a sintering density of 50-70% of the volume ratio.

The further processing of the anodes to capacitors takes place by "anodizing," i.e., electrochemical generation of the pentoxide layer in an electrolyte such as dilute phosphoric acid up to the desired anodization voltage, which is 1.5-4 times the voltage of the desired working voltage of the capacitor.

#### Test conditions

The production, molding and measurement of the anodes described in the following examples took place according to the following parameters, unless otherwise expressly described in the examples.

#### Anode production:

Weight without wire:	0.072 g
Diameter:	3.00 mm
Length:	3.25 mm
Pressed density:	3.14 g/cm <sup>3</sup>

**Anode sintering:**

1250°C	20 min
1450°C	20 min
1600°C	20 min

**Anodization:**

Forming voltage:	40 V or 60 V (see examples)
Formation current:	100 mA/g
Forming time:	2 h or 4 h (see examples)
Electrolyte:	0.1% H <sub>3</sub> PO <sub>4</sub> (conductivity at 25°C: 2.5 mS/cm)
Temperature:	80°C

**Measurement of capacitance**

Electrolyte:	18% H <sub>2</sub> SO <sub>4</sub>
Temperature:	23°C
Frequency:	120 Hz
Bias:	1.5 V (if applied)

**Measurement of leakage current:**

Electrolyte:	18% H <sub>2</sub> SO <sub>4</sub>
Temperature:	23°C
Charge time:	2 min
Voltage:	70% of forming voltage (28 or 42 V)

**Example 1**

A niobium-vanadium alloy containing 0.894% vanadium was produced as follows: 897.9 g niobium oxide hydrate Nb<sub>2</sub>O<sub>5</sub>·xH<sub>2</sub>O (Nb<sub>2</sub>O<sub>5</sub> content 63.09%) was thoroughly mixed with 9.2 g ammonium metavanadate NH<sub>4</sub>VO<sub>3</sub> dissolved in 1000 mL H<sub>2</sub>O, then dried at 110°C for 24 h and then calcined for 3.5 h at 950°C. The Nb<sub>2</sub>O<sub>5</sub> · x H<sub>2</sub>O has a primary particle size of about 600 nm. The mixed oxide prepared in this way was then packed into molybdenum boats and held for 4 h at 1450°C under a slow flowing hydrogen atmosphere. The resulting suboxide had the composition NbO<sub>2</sub> (X-ray diffraction) and contains 0.716% vanadium. The product was then put on a fine-mesh grating, under which was arranged a crucible containing magnesium in a 1.1-fold stoichiometric amount with respect to the oxygen content of the suboxide, and heated under argon to 1000°C for 6 h. In doing so the magnesium evaporated and reacted with the

suboxide lying above. After cooling the oven to room temperature, air was slowly supplied in order to passivate the metal surface. The reduction material was then washed with sulfuric acid, washed with demineralized water until neutral and dried.

Analysis of the niobium powder gave the following content:

V 8940 ppm

O 15,000 ppm (3289 ppm/m<sup>2</sup>)

N 342 ppm

Mg 190 ppm

C 33 ppm

Fe, Cr, Ni, Al, Ta each <20 ppm

The specific BET surface of the powder was 4.56 m<sup>2</sup>/g. The X-ray diffraction showed only reflections slightly shifted toward smaller angles, which points to a solid solution of vanadium in niobium.

Anodes were produced from this Nb-V alloy powder (powder A) and from a niobium powder produced by published proposals of the applicant in accordance with DE 19831280 A1 (powder B, comparison pattern) with the following contents:

V <1 ppm

O 16,000 ppm (3883 ppm/m<sup>2</sup>)

N 180 ppm

Mg 300 ppm

Σ (Fe, Cr, Ni) <15 ppm

C 14 ppm

with a specific BET surface of 4.32 m<sup>2</sup>/g, sintered at 1150°C and formed at 40 V. The specific BET surface (Quantasorb) was determined to be 0.83 + 0.2 m<sup>2</sup>/g on some of the anodes before forming.

Tables 1 and 2 show the measurement of the specific capacitances for anodes of the two powders in different electrolytes at different bias voltages:

Table 1  
Measurement in 18% H<sub>2</sub>SO<sub>4</sub>

Elektrolyt ①	Pulver A ②			Pulver B ②		
BIAS	0 V	2 V	4 V	0 V	2 V	4 V
③ gem. Kapazität $\mu\text{F}$	241	241	241	881	238	235
spez. Kapazität $\mu\text{FV/g}$	133889	133889	133889	489444	132222	130556
gem. Reststrom $\mu\text{A}$	2.97			3.04		
spez. Reststrom $\text{nA}/\mu\text{FV}$	0.31	0.31	0.31	0.09	0.32	0.32

Key: 1 Electrolyte  
 2 Powder \_\_\_\_\_  
 3 Measured capacitance  $\mu\text{F}$   
 Specific capacitance  $\mu\text{FV/g}$   
 Measured leakage current  $\mu\text{A}$   
 Specific leakage current  $\text{nA}/\mu\text{FV}$

Table 2  
Measurement in 10% H<sub>3</sub>PO<sub>4</sub>

Elektrolyt ①	Pulver A ②			Pulver B ②		
BIAS	0 V	2 V	4 V	0 V	2 V	4 V
③ gem. Kapazität $\mu\text{F}$	159	159	159	559	151	149
spez. Kapazität $\mu\text{FV/g}$	88333	88333	88333	310556	83889	82778
gem. Reststrom $\mu\text{A}$	2.72			2.81		
spez. Reststrom $\text{nA}/\mu\text{FV}$	0.43	0.43	0.43	0.13	0.47	0.47

Key: 1 Electrolyte  
 2 Powder \_\_\_\_\_  
 3 Measured capacitance  $\mu\text{F}$   
 Specific capacitance  $\mu\text{FV/g}$   
 Measured leakage current  $\mu\text{A}$   
 Specific leakage current  $\text{nA}/\mu\text{FV}$

### Example 2

A niobium tantalum vanadium alloy containing 1.26% vanadium was produced as follows: 1104.3 g niobium oxide hydrate  $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  ( $\text{Nb}_2\text{O}_5$  content 67.1%) were thoroughly mixed with 322.7 g tantalum oxide hydrate  $\text{Ta}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  ( $\text{Ta}_2\text{O}_5$  content 75.4%) and 28.93 g ammonium metavanadate  $\text{NH}_4\text{VO}_3$ , then dried for 24 h at 110°C and then calcined for 12 h at

1150°C. The mixed oxide prepared in this way was then packed into molybdenum boats and held for 6 h under a slow stream of hydrogen at 1500°C. The resulting suboxide had the composition NbO<sub>2</sub> (X-ray diffraction shows reflection for NbO<sub>2</sub> shifted only toward smaller angles) and contained 21.13% tantalum and 1.05% vanadium. The product was then put on a fine-mesh grating, under which there was a crucible containing magnesium in a 1.2-fold stoichiometric amount with respect to the oxygen content of the suboxide, and was heated to 1050°C under argon for 4 h. In doing so the magnesium evaporated and reacted with the suboxide above it. After cooling the oven to room temperature air was slowly admitted to the metal surface for passivation. The reduction material was then washed with sulfuric acid and then washed until neutral with demineralized water and dried.

The analysis of the Nb-Ta/V alloy powder gave a content of:

Ta 24.33%

V 12,600 ppm

O 12,325 ppm (3322 ppm/mm<sup>2</sup>)

N 92 ppm

Mg 45 ppm

C 24 ppm

Fe, Cr, Ni, Al each <20 ppm

The specific BET surface of the powder was 3.71 m<sup>2</sup>/g. The X-ray diffraction powder showed reflections for niobium only slightly shifted toward smaller angles, which points to a solid solution of tantalum and vanadium in niobium.

Anodes were prepared from this Nb-Ta-V alloy powder (powder A) and from an analogous niobium-tantalum alloy powder that was prepared without the ammonium metavanadate (powder B, comparison sample) with the following contents:

Ta 22.14%

V <1 ppm

O 13,120 ppm (3390 ppm/m<sup>2</sup>)

N 112 ppm

Mg 67 ppm

Σ (Fe, Cr, Ni) <15 ppm

C 41 ppm

and a specific BET surface of 3.87 m<sup>2</sup>/g, sintered at 1200°C and formed at 40 V. Before forming the specific BET surface was determined (quantasorb) to be 0.91 ± 0.4 m<sup>2</sup>/g on a few of the anodes.

Tables 3 and 4 show the measurement of the specific capacitances for anodes made from both powders in different electrolytes at different bias voltages:

Table 3  
Measurement in 18% H<sub>2</sub>SO<sub>4</sub>

Elektrolyt ①	Pulver A ②			Pulver B ②		
BIAS	0 V	2 V	4 V	0 V	2 V	4 V
③ gem. Kapazität $\mu\text{F}$	379	379	379	1319	372	367
spez. Kapazität $\mu\text{FV/g}$	210556	210556	210556	732778	206667	203889
gem. Reststrom $\mu\text{A}$	7.0			8.4		
spez. Reststrom $\text{nA}/\mu\text{FV}$	0.46	0.46	0.46	0.16	0.56	0.57

Key: 1 Electrolyte  
 2 Powder \_\_\_\_\_  
 3 Measured capacitance  $\mu\text{F}$   
 Specific capacitance  $\mu\text{FV/g}$   
 Measured leakage current  $\mu\text{A}$   
 Specific leakage current  $\text{nA}/\mu\text{FV}$

Table 4  
Measurement in 10% H<sub>3</sub>PO<sub>4</sub>

Elektrolyt ①	Pulver A ②			Pulver B ②		
BIAS	0 V	2 V	4 V	0 V	2 V	4 V
③ gem. Kapazität $\mu\text{F}$	237	237	237	859	231	227
spez. Kapazität $\mu\text{FV/g}$	131667	131667	131667	477222	128333	126111
gem. Reststrom $\mu\text{A}$	6.2			6.5		
spez. Reststrom $\text{nA}/\mu\text{FV}$	0.65	0.65	0.65	0.19	0.70	0.72

Key: 1 Electrolyte  
 2 Powder \_\_\_\_\_  
 3 Measured capacitance  $\mu\text{F}$   
 Specific capacitance  $\mu\text{FV/g}$   
 Measured leakage current  $\mu\text{A}$   
 Specific leakage current  $\text{nA}/\mu\text{FV}$

Example 3

A vanadium-doped niobium(II) oxide (powder A) was produced as follows: 657.3 g of a niobium vanadium alloy powder produced as in Example 1, with the following purity and physical properties:

V 6047 ppm

O 14,500ppm

Mg 380 ppm

C 44 ppm

$\Sigma$  (Fe, Cr, Ni, Al, Ta) <25 ppm

C 79 ppm

specific BET surface  $4.34 \text{ m}^2/\text{g}$ , bulk weight according to Scott  $14.3 \text{ g/inch}^3$ , Hall flow flowability 22 sec, particle size determination by Mastersizer D10 = 65.1, D50 = 170.7, D90 = 292.7  $\mu\text{m}$

was thoroughly mixed with 566.5 g niobium pentoxide  $\text{Nb}_2\text{O}_5$  < 45  $\mu\text{m}$  having the following composition:

$\Sigma$  (Al, As, Ca, Co, Cr, Cu, Fe, Ga, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Si, Sn, Ta, Ti, W, V, Zr) <25 ppm

C < 10 ppm

S < 10 ppm

and put into a molybdenum boat. The boat was then heated to  $1250^\circ\text{C}$  for 6 h under a mild stream of hydrogen. The resulting product (sample A) had the composition NbO and showed the following contents and physical characteristics:

V 3110 ppm

O 14.71%

Mg 90 ppm

C 14 ppm

$\Sigma$  (Fe, Cr, Ni, Al, Ta) < 15 ppm

N 45 ppm

specific BET surface  $2.31 \text{ m}^2/\text{g}$ , bulk weight according to Scott  $13.9 \text{ g/inch}^3$ , Hall flow flowability 29 sec, particle size determination by Mastersizer D10 = 22.3, D50 = 123.4, D90 = 212.7  $\mu\text{m}$ .

Analogously a comparison sample was produced from a niobium powder produced according to published proposals of the applicant in accordance with DE 19831280 A1, having the following contents and physical properties:

V < 1 ppm



O 13,200 ppm

Mg 386 ppm

C 47 ppm

$\Sigma$  (Fe, Cr, Ni, Al, Ta) < 25 ppm

N 84 ppm

specific BET surface  $4.01 \text{ m}^2/\text{g}$ , bulk weight according to Scott  $13.6 \text{ g/inch}^3$ , hall flow flowability 30 sec, particle size determination by Mastersizer D10 = 44.7, D50 = 156.2, D90 = 283.9  $\mu\text{m}$ .

and a niobium pentoxide  $\text{Nb}_2\text{O}_5$  < 45  $\mu\text{m}$  with the following contents:

$\Sigma$  (Al, As, Ca, Co, Cr, Cu, Fe, Ga, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Si, Sn, Ta, Ti, W, V, Zr) < 25 ppm

C < 10 ppm

S < 10 ppm

an undoped niobium(II) oxide NbO (powder B) with the following purity and physical properties:

V < 1 ppm

O 14.62%

Mg 54 ppm

C 14 ppm

$\Sigma$  (Fe, Cr, Ni, Al, Ta) < 20 ppm

N 56 ppm

specific BET surface  $2.47 \text{ m}^2/\text{g}$ , bulk weight according to Scott  $13.6 \text{ g/inch}^3$ , hall flow flowability 30 sec, particle size determination by Mastersizer D10 = 27.7, D50 = 131.9, D90 = 221.1  $\mu\text{m}$ .

Anodes were pressed from both powders, sintered for 20 min at  $1350^\circ\text{C}$  and formed at 40 V. Table 5 shows the measurement of the specific capacitances for anodes of the two powders in 18%  $\text{H}_2\text{SO}_4$  at various bias voltages.

Elektrolyt ①	Pulver A ②			Pulver B ②		
BIAS	0 V	2 V	4 V	0 V	2 V	4 V
③ gem. Kapazität $\mu\text{F}$	346	346	346	1261	349	341
spez. Kapazität $\mu\text{FV/g}$	192222	192222	192222	700556	193889	189444
gem. Reststrom $\mu\text{A}$	1.1			1.3		
spez. Reststrom $\text{nA}/\mu\text{FV}$	0.08	0.08	0.08	0.03	0.09	0.10

- Key: 1 Electrolyte  
 2 Powder \_\_\_\_\_  
 3 Measured capacitance  $\mu\text{F}$   
 Specific capacitance  $\mu\text{FV/g}$   
 Measured leakage current  $\mu\text{A}$   
 Specific leakage current  $\text{nA}/\mu\text{FV}$

#### Example 4

Niobium powders with various vanadium contents were produced in accordance with Example 1 (see table below, powders 2-6). Anodes were produced from these powders and from a niobium powder produced in accordance with DE 198 31 280 A1 (see table below, powder 1), sintered at  $1150^\circ\text{C}$  and then formed at 40 V.

The following table shows the results of capacitance measurements for anodes of all six powders made with and without 2.0 V applied bias voltage.

	1	2	3	4	5	6
O ppm	13800	12000	15100	14800	15300	13200
N ppm	<300	<300	<300	<300	<300	<300
H ppm	225	189	315	237	262	201
C ppm	36	25	29	35	28	31
$\Sigma$ (Fe, Cr, Ni)	9	7	9	6	8	8
Mg ppm	135	195	94	130	160	155
V ppm	<1	77	298	371	644	942
① BET-Oberfläche $\text{m}^2/\text{g}$	4,01	3,39	4,36	4,11	4,21	3,53
② gem. Kapazität $\mu\text{F}$ ohne Bias	680	400	214	206	209	198
③ gem. Kapazität $\mu\text{F}$ mit Bias	214	194	205	200	207	198
④ spez. Kapazität $\mu\text{FV/g}$	119450	107780	113890	111100	115000	110000
⑤ gem. Reststrom $\mu\text{A}$	4,4	4,2	4,3	4,7	4,1	4,0
⑥ spez. Reststrom $\mu\text{A/g}$	62	58	61	65	57	56

- Key: 1 BET surface,  $\text{m}^2/\text{g}$   
 2 Measured capacitance,  $\mu\text{F}$  without bias  
 3 Measured capacitance,  $\mu\text{F}$  with bias  
 4 Specific capacitance  $\mu\text{FV/g}$   
 5 Measured leakage current  $\mu\text{A}$   
 6 Specific leakage current  $\text{nA/g}$

### Claims

1. A capacitor with a niobium-based anode with bias-independent capacitance.
2. A capacitor as in Claim 1 with a niobium-based anode and a barrier layer based on niobium pentoxide, which is characterized by a content of vanadium at least in the barrier layer.
3. A capacitor as in Claim 2, with a vanadium content from 10 to 100,000 ppm.
4. A capacitor as in Claim 3, with a vanadium content from 500 to 10,000 ppm.
5. A capacitor as in one of Claims 1-4, where the anode consists of niobium metal, niobium suboxide, niobium nitride and/or niobium oxynitride.
6. A capacitor as in one of Claims 1-4, where the anode consists of a niobium-tantalum alloy.
7. A capacitor as in Claim 5, where the anode consists of a niobium core and a suboxide layer.
8. A capacitor as in one of Claims 5-7, where the anode contains 10-100,000 ppm of vanadium.
9. A capacitor as in Claim 8, where the anode contains 500-10,000 ppm vanadium.
10. A capacitor as in one of Claims 5-7, where the barrier layer contains 10-10,000 ppm vanadium with respect to the total anode mass.
11. A niobium-based anode with bias-independent capacitance.
12. A niobium-based anode containing 10-100,000 ppm vanadium.
13. An anode as in Claim 11, containing 10-100,000 ppm vanadium.
14. An anode based on niobium and/or niobium compounds containing a surface coating of 10-10,000 ppm vanadium with respect to the anode.
15. Niobium-based powders containing 10-100,000 ppm vanadium.
16. Niobium-based powders containing 500-10,000 ppm vanadium.
17. A method for producing vanadium-containing niobium-based powders, which is characterized by the fact that vanadium powder, vanadium oxide and/or a vanadium compound that can be decomposed to vanadium oxide by hydrolysis or thermally is mixed with a niobium metal, niobium oxide and/or niobium oxide hydrate, the mixture is optionally dried and calcined, and the mixed oxide is reduced to vanadium-containing niobium suboxide or niobium metal and optionally nitrided.
18. A method as in Claim 16 [sic], which is characterized by the fact that the reduction of the vanadium-containing mixed oxide to vanadium-containing NbO<sub>2</sub> is carried out in a stream of hydrogen at a temperature from 1000-1500°C.

19. A method as in Claim 16 or 17 [sic], which is characterized by the fact that the conversion of the vanadium-containing  $\text{Nb}_2\text{O}_5$  or  $\text{NbO}_2$ , optionally also with vanadium-containing niobium powder, to vanadium-containing  $\text{NbO}$  is carried out by heating in a stream of hydrogen or a vacuum to 900-1600°C.

20. A method as in Claim 16 or 17 [sic], which is characterized by the fact that the reduction of the vanadium-containing niobium oxide to niobium metal is carried out by heating in the presence of magnesium vapor under a protective gas atmosphere.

21. A method as in one of Claims 16 [sic]-20, which is characterized by the fact that the nitriding is carried out by heating the vanadium-containing niobium metal or niobium suboxide powder in a nitrogen-containing atmosphere.

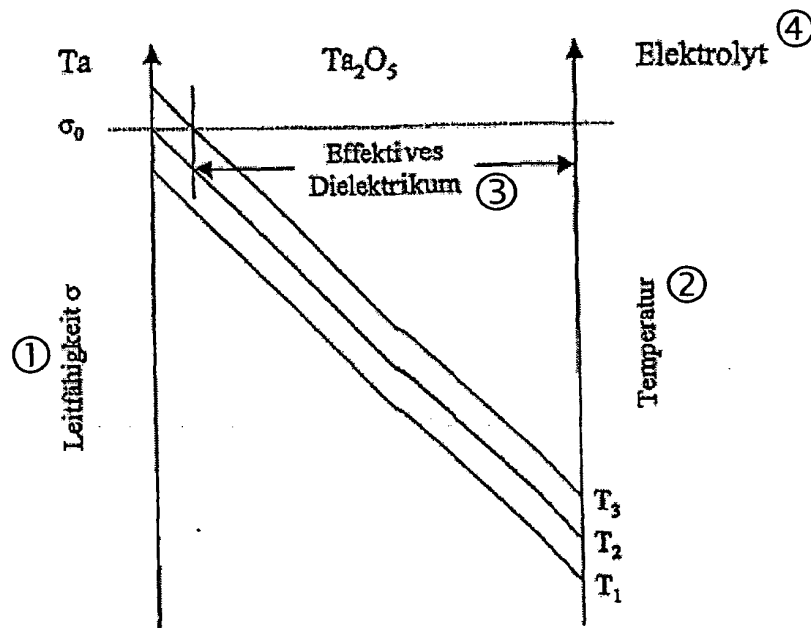


Figure 1

- Key: 1 Conductivity  $\sigma$   
 2 Temperature  
 3 Effective dielectric  
 4 Electrolyte

## INTERNATIONAL SEARCH REPORT

International Application No.  
PC1/cP 01/06525

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 H0169/052

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 H016 B22F C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 564 348 A (CHESELDINE DAVID M) 16 February 1971 (1971-02-16) column 2, line 70 - line 72	1-17
A	US 3 710 474 A (KELLY M ET AL) 16 January 1973 (1973-01-16) column 1, line 20 - line 38	1-17
A	US 3 984 208 A (ESCHER BALINT ET AL) 5 October 1976 (1976-10-05) claim 1	1-16
A	DE 26 36 279 B (STANDARD ELEKTRIK LORENZ AG) 8 June 1978 (1978-06-08) claim 1	1, 6, 12, 13, 15, 16

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

Continuation on patent family members

International Application No.

PCT/EP 01/06525

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